FORMATION OF VOLATILE PRECURSORS OF NO$_x$
IN THE RAPID PYROLYSIS OF NITROGEN-CONTAINING HETEROAROMATICS

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INTRODUCTION

Identification of the reaction pathways whereby fuel-bound nitrogen evolves as NO$_x$ in the combustion of low rank fuels has attracted considerable recent attention. As models for the evolution of NO$_x$ from coal combustion, compounds containing the six-membered heteroaromatic pyridine ring and the five-membered pyrrole ring are being investigated. Recently, we have studied the kinetics of pyrolysis of pyridine[1] by single pulse shock tube techniques and developed a detailed kinetic reaction mechanism to model the observed products of decomposition. Pyridine was found to decompose principally via a hydrogen chain mechanism involving abstraction of the ring hydrogen *ortho* to the nitrogen atom, followed by ring scission of the *o*-pyridyl radical to an open-chain radical which could eliminate acetylene and form the HC=CH-CN radical which may eliminate H and form cyanoacetylene or produce acrylonitrile via an abstraction route. HCN was found to be largely a secondary product of pyrolysis of these organic nitriles and also of acetonitrile.

More recently, our investigations of the kinetics of pyrolysis of pyrrole[2] have shown that the five-membered heterocycle decomposes very differently from the six-membered heteroaromatic. Isomerization followed by ring opening to the open-chain C$_3$H$_5$CN isomers of pyrrole predominates the mechanism. Our interpretation of the kinetics has assumed that the decomposition is initiated by the reversible tautomeric reaction
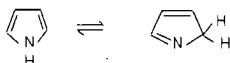
to form the 2-H pyrrole (pyrrolenine) with subsequent rupture of the weaker C2-N bond in the 2-H tautomer. It has been shown[2,3] that only through secondary decomposition of the C$_3$H$_5$CN products (principally cis- and trans- crotononitrile and allyl cyanide) are the NO$_x$ precursors including HCN produced. Thus, an understanding of the pathways of NO$_x$ formation from pyrrole rings requires a knowledge of the thermal decomposition kinetics of the C$_3$H$_5$CN isomers of pyrrole. This is considered in one part of this paper.

In heavy fuels heteroatoms are often found in condensed ring environments and in substituted rings rather than in the simple unsubstituted five- and six-membered rings. Evolution of NO$_x$ precursors might well depend upon the degree of heteroatomic ring substitution or condensation. The present work therefore involves, in part, a study of the simplest ring substituted heteroaromatic, 2-picoline (2-methylpyridine), the heteroaromatic analogue of toluene, whose stabilized radical, benzyl plays an important role in aromatic hydrocarbon pyrolyses and oxidations. Its heteroaromatic radical analogue, 2-picolyl might also be expected to be a key radical in heteroaromatic oxidations.

EXPERIMENTAL

Kinetics of pyrolysis of the nitrogen–containing products (cis– and trans–crotononitrile, allyl cyanide and 2–picoline) have been studied dilute in argon (0.1–0.4 mol%) in a single–pulse shock tube (SPST) over the temperature range 1100 to 1700 K, at pressures from 17–23 atm and at uniform residence times behind the reflected shock front of 600–800 μs. Analyses of products and remaining reactant have been made by capillary column GC. Product identifications have been made, where possible by comparison of retention times with standard samples, after initial identification by GC/MS and, in some cases, by FTIR spectrometry. The shock tube is equipped with pairs of UV–transmitting sapphire windows adjacent to the endwall. The absorption spectra of 2–picoline vapour and its products of decomposition have been measured over the wavelength range of 250–350 nm at a distance of 35 mm from the endwall with a detection system of time constant ≤5 μs. Details of the shock tube and ancillary analytical system are presented in our earlier publications.[1,2] Samples of each compound studied were purchased from Aldrich of 98–99% purity and were further purified by several bulb–to–bulb distillations to greater than 99.8% (by GC) in all cases. Pressures and temperatures behind the reflected shock were computed from measurements both of incident and reflected shock velocities.

RESULTS AND DISCUSSION

Secondary Decomposition of Pyrrole Pyrolysis Products

Figures 1(a)–(d) illustrate the temperature profiles of all products of significance for both allylcyanide and crotononitrile pyrolysis. The same set of products was observed irrespective of whether the initial reactant was allyl cyanide or crotononitrile, with only the relative yields of the products changing with starting isomer. HCN, acetylene, acetonitrile and acrylonitrile were all observed at very low extents of decomposition, and remained the major products at high extents of decomposition. Minor nitrogen–containing products were ethyl cyanide, cyanoacetylene, and cyanopropyne/cyanoallene. Methane was also present in significant concentrations, along with smaller quantities of ethylene, propene and propyne. Traces of the following compounds could also be detected: cis– and trans– 1-cyano(1,3-)butadiene, benzonitrile, pyridine, diacetylene, 1,3-butadiene, 1-butene, benzene and toluene. The major difference in product distributions between the reactants crotononitrile and allylcyanide was that allylcyanide yielded significantly higher proportions of HCN, acetonitrile, acetylene and ethylene. C_3 hydrocarbons were also generated in higher concentrations for allyl cyanide when compared with crotononitrile. No dependence of the rate of decomposition of the reactant on initial concentration was observed.

The product distribution observed in the pyrolysis of the butenenitriles can best be described in terms of a free radical mechanism. The observation of a mixture of C_3H_5CN isomers in the product mixture shows that isomerization of the starting isomers occurs simultaneously with decomposition. Although there are considerable uncertainties in the thermochemistry of some of the nitrogen–containing radicals produced, it would appear that the most likely initiation reaction for the free radical mechanism would occur through single C–C bond fission. For crotononitrile, C_3–C_4 bond fission [reaction (1)] would be expected to take place whereas with allyl cyanide C_2–C_3 fission (2) would be most favourable.

$$CH_3CHCHCN \rightarrow CH_3 + HC=CHCN \qquad (1)$$

$$H_2C=CHCH_2CN \rightarrow H_2C=CH + CH_2CN \qquad (2)$$

Although initiation through C–H bond fission is possible, the significantly higher C–H bond energy

would make this only a minor initiation pathway. Thermochemical parameters for radicals and other species of importance in this study are given in Table 1. In the Table certain of the heats of formation have been obtained from kinetic modeling of pyrolysis kinetics. Entropies and heat capacities have been obtained by approximate Third Law calculations.

Formation of the major products, acetylene and acetonitrile, can be modeled by means of a simple abstraction chain mechanism in which the abstacting radical is CH_2CN. See Figure 2. A major intermediate in this mechanism would appear to be the cyanoallyl radical, C_3H_4CN. Analogous with allyl itself, we would expect this radical to possess resonance stability. Fission of a C–C bond in this radical would seem less likely than rearrangement to a less stable radical whose bond fission leads to C_2H_2 and to regeneration of CH_2CN. Both vinyl and its cyano- analogue, cyanovinyl (HC=CHCN), should readily undergo unimolecular C–H fission, on the one hand to acetylene, on the other, to produce the observed cyanoacetylene. Hydrogen atom addition, either to the double bond of C_3H_5CN to to the nitrile group can produce another set of observed products, including the major products acrylonitrile and HCN. (See Figures 3 and 4). A detailed kinetic model comprising 107 reactions which include both abstractions and H additions as well as isomerization reactions of the C_3H_5CN isomers, has been used to satisfactorily model the major and minor products of the pyrolyses of crotononitrile and allyl cyanide.[4] Examples of the comparison between model predictions and experiment are given for some major products in Figure 5.

Pyrolysis of 2–picoline

2–Picoline may be considered to be the nitrogen heteroaromatic analogue of toluene. Behind reflected shock waves at residence times of about 800 μs and 20 atm, 2–picoline begins to dissociate at about 1250 K. Principal products of decomposition are HCN and C_2H_2 although cyanoacetylene, acrylonitrile and acetonitrile are significant nitrogen containing products. 2–Ethylpyridine and pyridine, especially at lower temperatures, are also observed. By analogy with toluene, we would expect the pyrolysis to be dominated by reactions of the 2–picolyl radical, the analogue of benzyl. Troe et al[5,6] have made an extensive investigation of the electronic absorption spectra of benzyl and benzyl decomposition fragments in both thermal and laser decomposition of toluene and side–chain substituted derivatives. They found that the spectral region around 300 nm in shock heated toluene is dominated by benzyl radical and benzyl products spectra.

Similarly we find the the absorption spectrum between 300–340 nm of shock heated 2–picoline is dominated by absorbing species which show strikingly similar temporal behaviour to those reported by Troe et al[5,6]. Figure 6 gives an example of the spectrum of decomposing 2–picoline vapour (0.2%) in argon at a temperature of 1634 K. Note the rapid rise in absorption to an initial steady state, followed by a longer time steady rise in absorption. The absorption is most probably the consequence of at least two absorbers, the first a species which undergoes rapid equilibration followed by slower decomposition to a more stable product or products. Similar observations in toluene decomposition have by attributed by Troe et al[5,6] to the initial formation of benzyl radicals which equilibrate rapidly owing to an unexpectedly high value of the rate constant for recombination

$$PhCH_2 + H \rightarrow PhCH_3 \qquad (-3)$$

Slower decomposition was attributed to homogeneous recombination of benzyl radicals to produce dibenzyl which eventually underwent successive H fissions to the highly absorbing molecule, stilbene.

It is therefore tempting in our 2–picoline studies to assign the initial absorber of 330 nm radiation to the 2–picolyl radical, which, like benzyl, must also undergo rapid recombination with H atoms. The slower increase in absorption would therefore be associated with 2–picolyl reaction products

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which are sufficiently conjugated to absorb strongly around 330 nm. It would seem that such chromophores are not very volatile since no absorption around 330 nm can be detected in the absorption spectra of the products when cooled to room temperature.

More work is required to establish that the initial carrier of 330 nm radiation is the 2-picolyl radical in the pyrolysis of 2-picoline. If, tentatively, we assume that the pyrolysis of 2-picoline is initiated by H atom fission to form 2-picolyl (reaction 3) then the value given in Table 1 for the heat of formation of this radical is in accord with our experiments. Values for the entropy and heat capacity of this radical have been obtained by a Third Law calculation in which vibrational frequencies of the radical have been estimated from those of toluene, benzyl and 2-picoline[5,7] and moments of inertia calculated from an estimated geometry.

ACKNOWLEDGEMENTS

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Table 1. Thermochemical data for nitrogen-containing compounds

Species	$\Delta H_{f,300}$ kcal/mol	$S_{f,300}$ cal/K /mol	C_p cal/K/mol					Ref.
			300	500	1000	1500	2000	
CH_2CN	59.0	59.8	12.3	15.5	20.2	22.6	29.3	8
$HC≡CHCN$	97.9	67.2	15.9	19.8	25.3	27.8	29.3	PW
$H_2C=CHCHCN$ (cyanoallyl)	77.0*	73.0	19.1	28.0	39.2	43.6	46.1	PW
$HC≡CHCH_2CN$	91.6*	80.3	21.1	28.0	39.2	42.7	45.4	PW
$H_3CCH=CHCN$	85.0*	76.5	22.3	32.1	45.5	51.0	54.4	PW
$H_3CCH=CHCH=N·$	80.6	76.5	22.3	32.1	45.5	51.0	54.4	PW
Py·	81.7*	72.6	18.0	28.9	42.8	48.5	51.1	1
$PyCH_2$[b]	65*	78.1	25.4	38.9	56.4	63.8	67.5	PW

[a]ortho-pyridyl radical   [b]ortho-picolyl radical   PW: present work
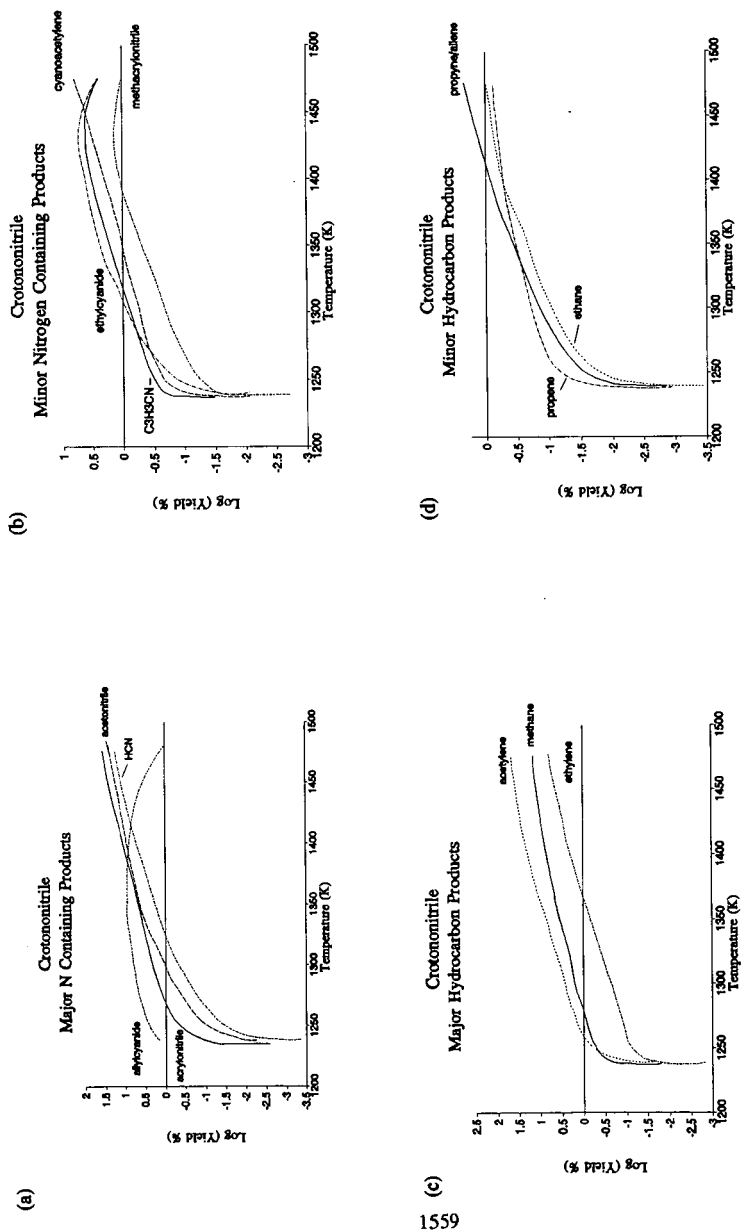*Value derived from kinetic modeling.

(a)

Crotononitrile
Major N Containing Products

Log (Yield %)

Temperature (K)

acetonitrile

HCN

ethylcyanide

acrylonitrile

(b)

Crotononitrile
Minor Nitrogen Containing Products

Log (Yield %)

Temperature (K)

cyanoacetylene

methacrylonitrile

ethylcyanide

C3H3CN

(c)

Crotononitrile
Major Hydrocarbon Products

Log (Yield %)

Temperature (K)

acetylene

methane

ethylene

(d)

Crotononitrile
Minor Hydrocarbon Products

Log (Yield %)

Temperature (K)

propyne/allene

ethane

propane

Figure 1. Products of pyrolysis of crotononitrile.

Figure 4. H additions to the nitrile group

Figure 3. H additions across the double bond

Figure 2. Free radical chain mechanisms.

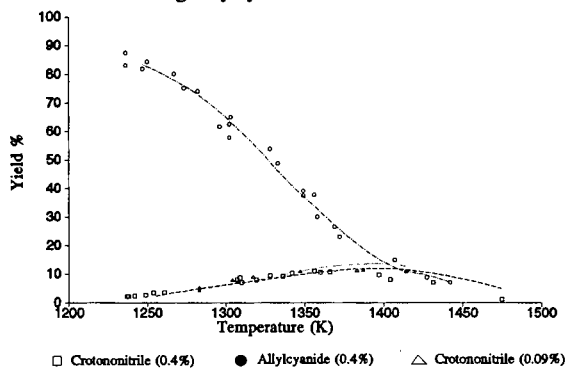## Butenenitrile Pyrolysis
Modeling Allylcyanide Concentration

Figure 5(a). Modeling of Allylcyanide Concentration :
(points indicate experimental values , lines model predictions.)

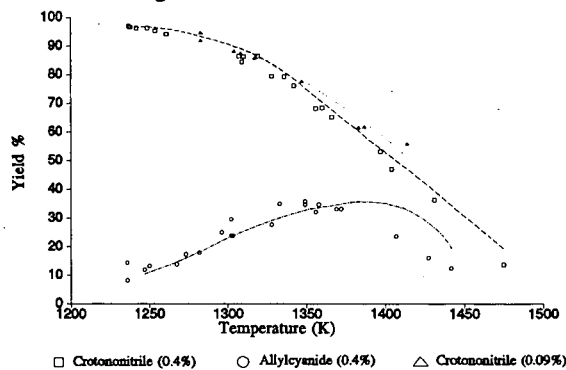## Butenenitrile Pyrolysis
Modeling of Crotononitrile Concentration

Figure 5(b). Modeling of Crotononitrile Concentration :
(points indicate experimental values , lines model predictions.)

Butenenitrile Pyrolysis
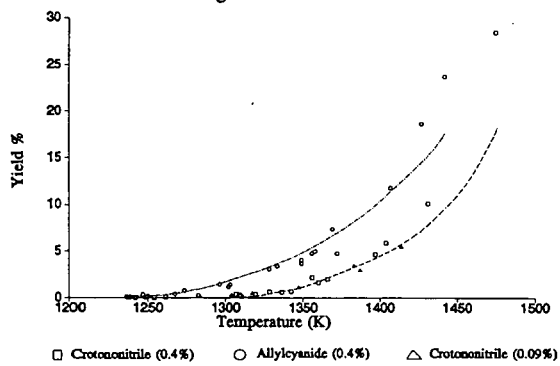## Modeling of HCN Formation

Figure 5(c). Modeling of HCN Formation :
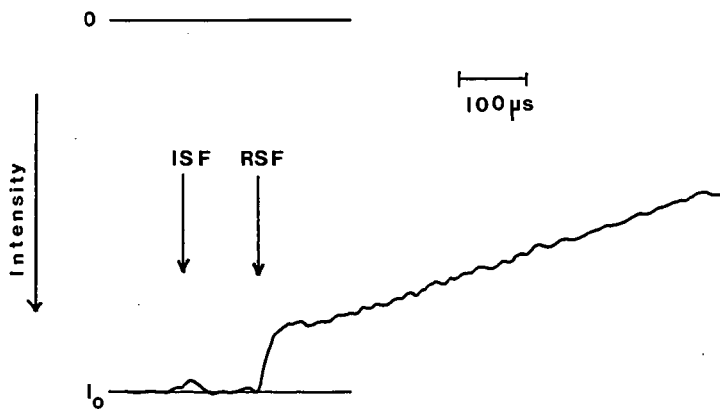(points indicate experimental values ; lines model predictions.)

Figure 6. Time dependence of an oscilloscope trace recording the absorption of 330 nm radiation in the pyrolysis of 2-picoline at 1634 K and 20 atm. ISF denotes the arrival of the incident shock front at the observation window, RSF denotes reflected shock front.